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## TRANSPARENT CONDUCTIVE OXIDES FOR PLASTIC FLAT PANEL DISPLAYS

### 5 CROSS-REFERENCE TO RELATED APPLICATIONS

This application claims the benefit of U.S. Provisional Application No. 60/106,871, filed December 29, 1998. Further, this application incorporates by reference the content of the following: U.S. Patent No. 5,440,446, issued August 8, 1995, U.S. Patent No. 5,725,909, issued March 10, 1998, U.S. Patent Application No. 10 08/706,180, filed August 30, 1996, and U.S. Patent Application No. 08/741,609, filed October 31, 1996.

### FIELD OF THE INVENTION

This invention relates to composite substrates for flat panel displays (FPD), packaging materials and light sources (electro luminescence lamps) comprising a plastic substrate having thin film barrier and electrode layers, in particular, multiple thin alternating layers of metallic film, transparent conductive oxide (TCO), metal nitride, and organic polymers deposited over the plastic substrate.

### 20 BACKGROUND OF THE INVENTION

The use of portable electronic devices incorporating flat panel displays is prevalent and increasing rapidly. Because of the portable nature of these devices, it is desired to minimize both the size and weight. The display portion of the device is generally larger and denser as compared to the rest of the device, and is manufactured on glass substrates. Accordingly, a smaller and lighter portable electronic device is most effectively achieved with a smaller and lighter electronic device display.

Despite being lightweight, plastic has not been considered a viable substrate material to be used for the manufacture of flat panel displays for multiple reasons. Most importantly, plastic substrates tend to fail prematurely due to degradation of the display medium. In particular, the display medium becomes degraded when atmospheric oxygen and water permeate the barrier layers and chemically degrade the conductive portion of the display matrix, generally comprised of liquid crystals and/or light emitting devices. Second, optical quality plastic substrates have limited thermal properties. In particular, there is a limited temperature range that allows useful optical quality (e.g.

clarity, transparency, uniform index of refraction) to be maintained, while maintaining the requisite mechanical strength and properties of the substrate.

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## SUMMARY OF THE INVENTION

The present invention is directed to the fabrication of flat panel displays on lightweight, flexible, plastic substrates. Because plastic substrates for FPDs are smaller and lighter than glass substrates, the electronic device with the plastic FPD is more portable, space-efficient and lightweight. In addition, electro luminescent devices fabricated on flexible polymeric substrates in a coating process have lower manufacturing costs than those with glass substrates, and improved ruggedness.

A display medium of the flat panel display is sandwiched between two electrode layers. At least one of the electrodes is transparent for viewing of the display. The display medium must be protected from oxidized degradation. In the present invention, at least one layer, having both barrier characteristics and the ability to function as an electrode, is deposited over the substrate. In particular, the layer has both low oxygen and moisture permeability, and a low enough resistivity to function as an electrode for the display. If lower permeability and/or higher conductivity is required, multiple alternating layers of barrier materials and conductive materials can be applied, however, the conductive layers may need contact. The barrier material may include an organic polymer, a transparent dielectric and/or a transparent conductive oxide. The conductive material may include a thin transparent conductive oxide, a thin transparent metallic film and/or a metal nitride.

25 Using a smoothing base coat layer over the plastic substrate imparts good optical quality throughout the substrate layers and provides a pristine surface for nucleation of the deposited conductive, e.g. TCO. The pristine surface smooths over any surface roughness of the plastic substrate, thereby adding to the FPD lifetime and optical quality.

30 While the smoothing layer may be applied by many well known non-vacuum liquid coating processes, e.g. Gravure, preferably, the base coat is fabricated through a polymer multilayer (PML) coating process. Related desirable coating processes are disclosed in U.S. Patents 5,547,508, 5,395,644, 5,260,095, Application number 08/939,594, entitled "*Plasma enhanced chemical deposition with low vapor pressure compounds*" herein incorporated by reference, *Thin Film Processes II*, edited by John

L. Vussen and Werner Kern, Academic Press, 1991, ISBN 0-12-728251-3, *Deposition Technologies for Films and Coatings, Developments and Applications*, Rointan F.

5 Bunshah et al, Noyes Publications, 1982, ISBN 0-8155-0906-5. Plasma PML processes are called liquid multilayer (LML) processes. The PML process for vacuum evaporation is used to deposit organic monomers over the plastic substrate. The organic monomer is then polymerized in-situ by electron beam or UV polymerization. The PML process is compatible with vapor deposition processes for layers such as TCO 10 layers. Both processes can be carried out in combined sequences within a single vacuum chamber, however, multiple vacuum chambers may be used. The PML deposited organic polymer layer is used to produce substrate surface smoothing and improve barrier coatings in the multilayer structure. The benefit of a smooth substrate 15 surface is that there is a clean surface for adhesion, nucleation, and growth of a deposited conductive layer, e.g. a TCO. Additionally, a PML deposited organic polymer layer provides protection of an underlying barrier layer in order to minimize holes in the layer so that there is low permeability.

A single layer coating with metal oxide layers, such as thin film dielectric coatings (alumina or silica or other certain metal oxides), or thick metallic film layers having 20 optical densities greater than 2.0 on plastic flat panel displays does not render low enough permeability for the processing and manufacture of these displays. Even where multiple layers of dielectrics, metals or the combination thereof are used, the improvement in performance is minimal. In order to provide barrier properties sufficient 25 for optical quality plastic flat panel displays, a transparent dielectric barrier, such as  $\text{SiO}_{2-x}$  or  $\text{Al}_2\text{O}_{3-y}$ , is deposited over a plastic substrate. When dielectric layers are combined with PML deposited organic polymer layers, outstanding barrier properties are achieved on flexible plastic substrates. Alternatively to the dielectric layer, a barrier coating of ITO (called "indium tin oxide", which is actually "Tin doped indium oxide," a mixture of indium oxide and tin oxide) or another TCO barrier is deposited over the 30 substrate. In yet another alternative embodiment, both TCO barrier layers and PML processed organic polymer layers are deposited over the plastic substrate. Moreover, in yet another alternative, both TCO barrier layers with PML processed organic polymer layers and the transparent dielectric barrier layers are deposited over the plastic or polymeric substrate. Multi layer structures of such organic and inorganic layers

5 deposited over a plastic substrate exhibit significantly improved barrier properties as compared to inorganic layers alone, or layers deposited over a glass substrate.

10 In a preferred embodiment, a PML processed top coat barrier polymer layer is applied before the previously deposited layer contacts a surface, such as a roller, thereby protecting the previously deposited layer. The PML processed top coat enhances the exclusion of moisture and atmospheric gases that chemically degrade the display medium and decrease the device performance.

15 Metal oxide dielectric barriers have previously been deposited by evaporation, sputtering, and chemical vapor deposition processes onto glass substrates. However, for achieving bulk like properties a high temperature deposition method must be used which would melt the plastic substrate, thereby negatively impacting the mechanical properties of the substrate. In the present invention, the PML process used for depositing an organic dielectric does not require such high temperatures and therefore does not significantly alter the mechanical properties of the substrate. However, organic polymer layers alone do not provide substantial barrier properties, particularly against water vapor.

20 When TCOs are deposited at low temperatures to accommodate the thermal and mechanical requirements of the substrate, the subsequent TCO coatings have less than bulk conductivity, i.e. low overall levels of conductivity. TCO films with a larger thickness deposited through this method achieve acceptable conductive levels for portable electronic devices. However, thick films of TCO are subject to cracking, crazing and, in some instances, delamination from the substrate, especially when they are processed 25 by a heat treatment step or a calendering process involving mechanical rollers (e.g. web coating). As a consequence, the TCO coating must be deposited in a series of thin layers, yet still maintain high conductive levels. Multiple thin layers of TCO avoid the problems associated with thicker layers, and can advantageously be electrically connected in parallel to provide adequate electrical performance characteristics.

30 The thin layers of TCO are preferably deposited in combination with the PML process, which leads to improved optical and electrical performance. Superior surface properties (low surface roughness, and high optical quality) and barrier properties (low vapor permeability) result when TCO coatings are deposited on a plastic substrate in combination with the PML process, and/or by providing hydrogen in the plasma of the 35 vacuum chamber used in the magnetron sputtering process of the TCO. Preferably,

moderate annealing temperature conditions are used for TCO deposition. The  
5 resistivity of ITO ("Tin doped indium oxide"), a TCO, is a function of the oxygen and tin  
content, as well as the deposition conditions (e.g. temperature). Previously, low  
temperature depositions yielded high resistivity ITO layers, when a low resistivity for ITO  
was desired. The resistivity of ITO was shown to decrease with a thicker TCO layer.  
But as discussed previously, thick TCO layers are prone to cracking or crazing. Multiple  
10 thin layers of TCO, as described in the present invention, will not crack and will yield a  
lower resistivity. Moreover, the surface resistivity of a thin film of TCO in multiple layers  
is low for a given film thickness, due to its improved microstructure.

In a preferred embodiment, a polymer smoothing coating is deposited over the  
substrate. The smoothing coating can be applied by a PML process or liquid coating.  
A TCO or metal layer is then deposited over the smoothing layer. Additionally, multiple  
15 alternating layers of a protective polymer layer and an additional TCO or metal layer is  
deposited. Preferably, the alternating layers are of the same material, e.g.  
TCO/polymer/TCO, etc.

In another preferred embodiment, a polymer smoothing coating layer is optionally  
deposited over the substrate. Additionally, multiple alternating layers of metal oxide and  
20 polymer layers are deposited over the substrate. A TCO layer is then deposited over  
the top of multiple alternating layers. These multiple alternating layers together with the  
TCO have adequate barrier and conductivity characteristics.

In yet another preferred embodiment, a substrate is coated with a TCO layer, a  
metal coating, and another TCO layer. This 3 layer configuration is called "optically  
25 enhanced metal," and has similar characteristics as a single TCO layer. With the  
optically enhanced metal good conductivity, transmission and barrier properties are  
achieved.

In still another preferred embodiment, a substrate is alternatively coated with an  
inorganic layer (such as TCO or dielectric metal oxides), and polymer layers to provide  
30 both barrier and conductive properties.

#### BRIEF DESCRIPTION OF THE DRAWINGS

The aspects of the present invention described above in summary and below in  
more detail as well as various advantageous aspects will become appreciated as the

same becomes better understood with reference to the specification, claims and drawings wherein:

5 FIG. 1 is a cross-sectional view of a composite substrate for a flat panel display (FPD) of the present invention;

FIG. 2 is a cross-sectional view of an embodiment of conductive barrier layer 3 of FIG. 1;

10 FIG. 3 is a cross-sectional view of another embodiment of conductive barrier layer 3 of FIG. 1;

FIG. 4 is a cross-sectional view of another embodiment of conductive barrier layer 3 of FIG. 1;

15 FIG. 5 is a cross-sectional view of another embodiment of conductive barrier layer 3 of FIG. 1;

FIG. 6 is a cross-sectional view of another embodiment of conductive barrier layer 3 of FIG. 1;

20 FIG. 7 is a cross-sectional view of another embodiment of conductive barrier layer 3 of FIG. 1;

FIG. 8 is a schematic illustration of a coating apparatus for forming the conductive barrier layer of FIG. 1;

25 FIG. 9a is a schematic illustration of a Tape automated bonding (TAB) process for the FPD of FIG. 1;

FIG. 9b is a cross-sectional view of the FPD before undergoing a bonding process;

30 FIG. 9c is a cross-sectional view of the FPD after undergoing a bonding process;

FIG. 10 is a chart showing water permeability of an ITO film deposited on a polyethylene terephthalate (PET) substrate versus ITO film sheet resistance;

FIG. 11 is a chart showing water permeability of ITO film deposited on a PET substrate versus ITO film thickness;

35 FIG. 12 is a chart showing oxygen permeability of ITO film deposited on a PET substrate versus ITO film thickness;

FIG. 13 is a chart showing oxygen permeability of ITO film deposited on a PET substrate versus ITO film sheet resistance;

FIG. 14 is a chart showing sheet resistance of various substrates versus oxygen flow rate through the respective substrate;

5 FIG. 15 is a chart showing resistivity of various substrates versus oxygen flow rate through the respective substrate;

10 FIG. 16 is a chart showing sheet resistance of various substrates versus oxygen flow rate through the respective substrate for 7.5% hydrogen in the plasma;

15 FIG. 17 is a chart showing resistivity of various substrates versus oxygen flow rate through the respective substrate for 7.5% hydrogen in the plasma;

20 FIG. 18 is a chart showing sheet resistance of various substrates versus oxygen flow rate through the respective substrate for 20% hydrogen in the plasma;

25 FIG. 19 is a chart showing resistivity of various substrates versus oxygen flow rate through the respective substrate for 20% hydrogen in the plasma;

30 FIG. 20 is a chart showing transmittance and reflectance spectra (for an ITO layer over a silver film layer over an ITO layer over a PET substrate at a sheet resistance of 14 Ohms/Square) versus wavelength;

35 FIG. 21 is a chart showing transmittance and reflectance spectra (for an ITO layer over a PET substrate at a sheet resistance of 29 Ohms/Square) versus wavelength;

40 FIG. 22 is a chart showing transmittance and reflectance spectra (for an ITO layer over a PET substrate at a sheet resistance of 57 Ohms/Square) versus wavelength;

45 FIG. 23 is a chart showing transmittance and reflectance spectra (for an ITO layer over a PET substrate at a sheet resistance of 65 Ohms/Square) versus wavelength; and

50 FIG. 24 is a chart showing transmittance and reflectance spectra (for an ITO layer over a PET substrate at a sheet resistance of 347 Ohms/Square) versus wavelength.

#### DETAILED DESCRIPTION OF THE INVENTION

55 A flat panel display (FPD) 1, of the present invention as shown in FIG. 1, employs lightweight, flexible, plastic substrates 38 for constructing FPDs. In between two plastic substrates of the flat panel display are at least two electrodes. At least one of the electrodes is transparent for viewing of the display. A display medium 2 for the flat panel display is situated between the two electrodes. The display medium must be protected from oxidized degradation.

5 The displays are fabricated using plastic substrates such as various polyolefins, e.g. polypropylene (PP), various polyesters, e.g. polyethylene terephthalate (PET), and other polymers such as polyethylene naphthalate (PEN), polyethersulphone (PES), polyestercarbonate (PC), polyetherimide (PEI), polyarylate (PAR), polyimide (PI), an polymers with trade name ARTON® (Japanese Synthetic Rubber Co., Tokyo, Japan) and AVATREL™ (B.F. Goodrich, Brecksville, Ohio). See Appendix A for deposition temperatures of the particular plastic substrate.

10 In the present invention, at least one layer, a conductive barrier layer 3 has both barrier characteristics (to protect the display medium) and the ability to function as an electrode, and is deposited over the substrate to form a composite substrate. In particular, layer 3 has both low oxygen and moisture permeability, and a low enough resistivity to function as an electrode for the display.

15 As shown in FIGs. 2 through 7, conductive barrier layer 3 comprises at least one sublayer 3<sup>1</sup> deposited over the substrate, for instance a single ITO layer. In a preferred embodiment, at least one pair of sublayers (a dyad of a polymer and a TCO, metal, or metal oxide) is deposited over the substrate. In an exemplary embodiment, multiple alternating sublayer pairs, comprised of the same materials as the original sublayer pair, are deposited over the substrate or over the previously deposited sublayer.

20 There are a myriad of possibilities for materials comprising the sublayers of the conductive barrier layer. FIGs. 2-7 illustrate only some of the more preferred embodiments of sublayer 3<sup>1</sup> materials for conductive barrier layer 3.

25 In a preferred embodiment, a polymer smoothing coating 20 is deposited over the substrate 38. The smoothing coating can be applied by a PML process or liquid coating to render a hardcoated PET substrate that is abrasion resistant. A TCO 22 or metal layer 12 is then deposited over the smoothing layer, as shown in FIG. 3. Additionally, multiple alternating layers of a protective polymer layer 24 and an additional TCO 22 or metal layer 12 can be additionally deposited, as represented by sublayer 3<sup>1</sup>. Preferably, the alternating layers are of the same material, e.g. TCO/polymer/TCO, etc. FIG. 2 illustrates the embodiment of polymer/TCO/polymer without base coat 20.

30 In another preferred embodiment, shown in FIG. 7, a polymer smoothing coating layer is optionally deposited over the substrate. Additionally, multiple alternating layers of a dielectric 17 and polymer layers 24 are deposited over the substrate 38. The

number of multiple alternating layers vary, and is represented here by 3<sup>1</sup>, sublayers of the conductive barrier layer 3. A TCO layer 22 is then deposited over the top of multiple 5 alternating layers. These multiple alternating layers together with the TCO have adequate barrier and conductivity characteristics as described in more detail below.

In yet another preferred embodiment, a substrate is coated with a TCO layer, a metal coating, and another TCO layer. This 3 layer configuration is called "optically 10 enhanced metal," and has similar characteristics as a single TCO layer. With the optically enhanced metal good conductivity, transmission and barrier properties are achieved. Deposited on these 3 layers is preferably a polymer layer 24, that is alternating with the 3 layers as illustrated by the sublayer deposited over the polymer in FIG. 6.

In still another preferred embodiment, a substrate is alternatively coated with an 15 inorganic layer (such as TCO or dielectric metal oxides), and polymer layers to provide both barrier and conductive properties.

Sublayer 3<sup>1</sup> materials that provide barrier properties are thin transparent metal 20 oxides 16, thin transparent metallic films 12. The polymers 24 enhance barrier properties by reducing the number of holes in the films upon which they are deposited. The metal oxide layers alternatively comprise dielectric layers 17 and/or transparent 25 conductive oxide layers 22. The thickness for these barrier layers are in the nanometer and angstrom range. The thickness for the PML deposited layers are in the micron range. For example, improved barrier coating occurs when a PML deposited organic polymer layer (a base coat), and/or a metal oxide layer is placed over the plastic substrate. See Tables 2 and 3.

Sublayer 3<sup>1</sup> materials that provide conductive properties include a thin TCO 22, a thin transparent metallic film 12 (such as aluminum, silver, copper, gold, platinum, palladium, and alloys thereof), and a metal nitride 14 (such as transition metal nitrides, 30 nitrides of Group III and Group IV elements of the Periodic Table, for example: gallium nitride, silicon nitride, and titanium nitride). The thickness for these conductive layers are in the nanometer and angstrom range. Preferably the TCO is formed by multiple thin layers deposited at a reduced voltage, so that a low resistivity can be achieved. Consequently, the TCO can function as both the electrode and a barrier.

In the preferred embodiment, there is a PML processed base coat 20 deposited 35 over the substrate as shown in FIG. 3. The base coat produces substrate smoothing,

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5 and more importantly, in combination with other layers, the base coat has surprisingly protection characteristics. The sublayers can be deposited in combination with the process illustrated in FIG. 8.

10 Using a smoothing base coat layer over the plastic substrate imparts good optical quality throughout the substrate layers and provides a pristine surface for nucleation of the deposited TCO electrode layer. The pristine surface smooths over any surface 15 roughness of the plastic substrate, thereby adding to the FPD lifetime and optical quality.

20 In an exemplary embodiment, one or more metal oxide layers are replaced with a TCO. When TCO coatings, including ITO ("Tin doped indium oxide"), cadmium oxides (CdSn<sub>2</sub>O<sub>4</sub>, CdGa<sub>2</sub>O<sub>4</sub>, CdIn<sub>2</sub>O<sub>4</sub>, CdSb<sub>2</sub>O<sub>6</sub>, CdGeO<sub>4</sub>), tin oxides, indium oxides (In<sub>2</sub>O<sub>3</sub>: Ga, 25 GaInO<sub>3</sub> (Sn, Ge), (GaIn)<sub>2</sub>O<sub>3</sub>), zinc oxides (ZnO(Al), ZnO(Ga), ZnSnO<sub>3</sub>, Zn<sub>2</sub>SnO<sub>4</sub>, Zn<sub>2</sub>In<sub>2</sub>O<sub>5</sub>, Zn<sub>3</sub>In<sub>2</sub>O<sub>6</sub>), and/or magnesium oxides (MgIn<sub>2</sub>O<sub>4</sub>, MgIn<sub>2</sub>O<sub>4</sub> - Zn<sub>2</sub>In<sub>2</sub>O<sub>5</sub>) are deposited on a plastic substrate at a low temperature, they have an amorphous micro structure. For characteristics of the above TCO materials, see Appendix B. The amorphous structure and oxygen deficiency of the TCO allow the TCO coating to exhibit 30 conductive properties and barrier properties similar to transparent dielectric barrier layers, such as types of silica or alumina. For a more thorough discussion of the properties of the TCO layers, see Appendix C: *Deposition and Properties of ITO and Other Transparent Conductive Coatings*, Clark I. Bright, 1996, herein incorporated by reference. Because of the oxygen deficiency, the barrier layers gather the oxygen and 35 keep the oxygen from passing through. Multiple thin layers of TCO function as a transparent electrode and a transparent barrier layer. The benefit of using TCO alternating with metallic film layers, besides the barrier properties, is that all the layers of the structure are conductive, thus improving conductivity.

30 In the preferred embodiment, a suitable apparatus for coating the substrate with conductive and barrier layers is illustrated schematically in FIG. 8. All of the coating equipment is positioned in a conventional vacuum chamber 36. A roll of polypropylene, polyester or other suitable plastic sheet is mounted on a pay-out reel 37. Plastic sheet 38 forming the substrate is wrapped around a first rotatable drum 39, and fed to a take-up reel 41. An idler roll 42 is employed, as appropriate, for guiding the sheet 35 material from the payout reel to the drum and/or to the take-up reel.

5 A flash evaporator 43 is mounted in proximity to the drum at a first coating station. The flash evaporator deposits a layer or film of acrylate monomer on the substrate sheet as it travels around the drum. After being coated with acrylate monomer the substrate sheet passes an irradiation station where the acrylate is irradiated by a source 44 such as an electron gun or source of ultraviolet radiation. The radiation or electron bombardment of the film induces polymerization of the acrylate monomer.

10 The sheet then preferably passes a sputtering station 46 where a coating of TCO is applied by magnetron sputtering. The sheet then passes another flash evaporator 47 where another layer of acrylate monomer is deposited over the TCO layer. This layer of monomer is cured by irradiation from an ultraviolet or electron beam source 48 adjacent the drum. Depending on whether a layer of acrylate is above or below the TCO layer, either of evaporators 43 or 47 may be used. Clearly, if the TCO layer is to be sandwiched between layers of acrylate, both evaporators and their respective radiation sources are used. In addition to magnetron sputtering, the TCO layer may be processed by one of thermal evaporation, chemical vapor deposition, plasma enhanced chemical vapor deposition, and electron beam evaporation. Chemical vapor deposition is a relatively high temperature process, and is therefore the least desirable for use with plastic substrates.

15 In an alternative embodiment, a liquid smoothing applicator 52 is mounted in proximity to the drum at a first coating station. The liquid smoothing applicator deposits a layer of acrylate over the substrate. Additionally, the sheet then passes sputtering station 46 where a coating of thin metal film, metal oxide, and/or metal nitride is applied by one of vacuum sputtering, vacuum metallizing, plasma assisted chemical vapor deposition, or electron beam evaporation. For example, silicon oxides may be deposited by a plasma vapor deposition process using an oxidizing or inert carrier gas.

20 The various layers described can be deposited in several processes in addition to vacuum coating techniques. For instance, the layers can be deposited through roll coating. Additionally, the layers can be deposited by an in line coating machine, whereby a conveyor belt runs the substrate to be coated past multiple coating stations). Further, the layers can be deposited by an intermittent motion machine. In addition, the layers on the substrate can be coated using a multitude of machines. For instance, the 35 plastic substrate can first be coated through atmospheric roll coating with a cured

polymer and subsequently coated by vacuum deposition, or liquid coated, such as Gravure coating.

5 For multiple layers of organic polymer coatings deposited in the PML process, take up reel 41 with the sheet wound thereon, can replace pay out reel 37, and the process is repeated as desired. The roll of sheet is removed from the vacuum system for use.

10 FIG. 9a illustrates a Tape automated bonding (TAB) process for the FPD where the coated plastic substrate and display medium are bonded together with an adhesive, pressure and temperature. FIGs. 9b and 9c are a cross-sectional views of the FPD before and after undergoing the bonding process, respectively. The TAB process is one of the alternate methods for bonding the layers to construct the FPD. Because the layers of the present invention are thin, cracking, crazing, and delamination are avoided using processing methods of this type. FIGs. 9b and 9c illustrate the flat panel display with a protective overcoat 4 and conductive adhesive particles of the display medium 2.

15 20 25 Transparent dielectric layers with good barrier properties and a high refractive index, such as metal oxides like silicon oxide or aluminum oxide, used in combination with thin, transparent metallic film layers provide a transparent conductive barrier coating. The metal oxide layers are deposited at specific thicknesses to optimize the optical performance (e.g. transmittance) of a particular display. Preferably, the thin metallic film layer is sandwiched in between layers of metal oxide. Multiple alternating layers of metal oxides, with their barrier properties, and the highly conductive metallic film layers provide increased barrier performance and conductivity of a particular display medium.

30 The optical and electrical performance of transparent conductive oxide coatings are also improved by mildly annealing the substrate. Even though the substrate was heated to a moderate temperature of only 65°C, the resistivity of the ITO was still low enough to effectively operate as an electrode, because of the thin layer of ITO. See the Experimental Results below.

35 Further the optical and electrical performance of TCO coatings are also improved by providing hydrogen in the plasma of the vacuum chamber used in the sputtering process of the TCO. Lower resistivity and more reliable processing are achieved by providing hydrogen in the plasma. Under the reducing conditions of the hydrogen

5 plasma, the resulting ITO layer is deficient in oxygen content, and thus has significantly improved conductivity. Additionally, the deposition of ITO is easier to control, and a more uniform layer of ITO results.

10 In an alternative embodiment, a thin conductive metal nitride layer can be substituted for one or more thin metallic film layers. Metal oxide or TCO layers are utilized with the metal nitride layer for enhancing both the optical and electrical performance characteristics. Metal nitrides have good gas barrier properties. However, if the metal nitride layer is too thin, the moisture and oxygen permeability is not lowered. Because of the higher optical transparency silicon nitride thin films, for example, are attractive candidates for flexible FPD as barrier layers for atmospheric gases.

15 In another alternative embodiment, at least one of the metallic film layers can be replaced with a polymer layer formed via the PML process.

## RESULTS OF CONDUCTED EXPERIMENTS

20 The plastic substrate for a flat panel display requires very low oxygen and water vapor permeability, a surface roughness much less than the barrier film thickness, a high Tg (the glass transition temperature) to allow a higher temperature and/or higher energy ITO deposition process, and a high transparency with low (ND, index of refraction) birefringence.

25 Defects in the coated layers limit the barrier properties. For instance, rough substrates, particulates, and roller contact damage the coated layers. Rough substrates with thin film barriers can be smoothed and prevented from damage by roller contact with an organic basecoat and polymer top coat multilayers, respectively.

30 Multiple layers of TCO's deposited on the substrate achieve lower surface resistivity than a single layer of TCO. Further, the multiple TCO layers act as electrodes connected in parallel. Using non-stoichiometric dielectric of a group including silicon oxides, aluminum oxides, and silicon nitrides, allow for the fabrication all efficient thin film barriers for flexible plastic films.

35 Measured data for films made of sputtered ITO exhibited exceptional barrier properties. The optical, electrical and barrier properties were measured for ITO sputter-deposited directly onto a PET substrate, and also measured with a PML acrylic base coat over the substrate before deposition of the ITO, in a roll-to-roll (web) coating process. See FIGS. 10-18, and descriptions of the Figures below. The typical

5 performance of a single ITO layer deposited on a base coated PET substrate is  $> 85\%$ T (Transmittance) and  $\leq 80$  ohms/square. The ITO layer has a thickness of 140 nm, while the PET substrate has a thickness of about 0.007". For the single layer ITO film, oxygen permeability ranged from 0.005 to 0.05 oxygen cc/m<sup>2</sup>/day, while the water permeability ranged from 0.005 to 0.05 g/m<sup>2</sup>/day.

10 FIG. 10 discloses a chart showing water permeability of ITO film, as well as ITO sandwiching a silver layer, each deposited on a PET substrate versus ITO film sheet resistance. No smoothing base coat was applied to the substrate in either case. First, the ITO layer was DC sputter deposited onto a PET substrate. The deposited ITO film is sputtered from a ceramic target in a web coater. The vertical lines shown connect the midpoints of the range of permeability results at each measured resistance for the ITO film sheet. The chart shows that the permeability dips to a minimal value of approximately 0.006 g/m<sup>2</sup> day at a resistance of about 60 ohms/square. The permeability reaches a maximum of approximately 0.21 g/m<sup>2</sup> day at a resistance of about 350 ohms/square. Second, for a silver layer sandwiched in between ITO film layers over the substrate, the approximate permeability range was 0.04 to 0.075 g/m<sup>2</sup> day for the sheet resistance at about 12 ohms/square. For a more thorough discussion of sheet resistivity in ohms/square, see Appendix C.

15 FIG. 11 discloses a chart showing water permeability of ITO film, as well as ITO sandwiching a silver layer, each deposited on a PET substrate versus ITO film sheet thickness. First, the ITO layer alone is analyzed in the same manner as above. The chart shows that the permeability dips to a minimal value of approximately 0.006 g/m<sup>2</sup> day at a thickness of about 120 nm. The permeability reaches a maximum of approximately 0.21 g/m<sup>2</sup> day at a thickness of about 40 nm. Second, for the substrate with the sandwiched silver layer, the approximate permeability range was 0.04 to 0.075 g/m<sup>2</sup> day for a sheet thickness of approximately 120 nm.

20 FIGs. 12 and 13 disclose charts showing oxygen permeability of ITO film deposited on a PET substrate versus ITO film sheet thickness and sheet resistivity, respectively. FIG. 12 shows that the permeability dips to a minimal value of approximately 0.017 g/m<sup>2</sup> day at a thickness of about 220 nm. The permeability reaches a maximum of approximately 0.9 cc/m<sup>2</sup> day at a thickness of about 40 nm.

25 As shown Table 1, alternating barrier layers of PML deposited organic polymers and dielectrics have permeation rates below the limits of the instruments, which is 0.005

5 g/m<sup>2</sup>\*day for Permatran-W 3/31, an instrument for measuring water vapor transmission rates and 0.005 cc/m<sup>2</sup>\*day for Ox-Tran 2/20, an instrument for measuring oxygen transmission rates.

10 A transparent dielectric barrier layer or a "single layer" of TCO deposited on the substrate meets the barrier requirements for the plastic FPD. Barrier requirements vary by the type of display technology, liquid crystal display (LCD), organic light emitting display (OLED) and field emission display (FED). The acceptable value of vapor permeation with plastic substrates for FPD depends on the sensitivity of the specific display technology utilized. For example, the LCD is much less sensitive to vapor permeation than the OLED or FED. For the LCD, permeability in the range of 0.01 to 0.1 cc/m<sup>2</sup>\*day is needed for oxygen, but permeability in the range of 0.01 to 0.1 g/m<sup>2</sup> \*day is needed for water vapor. For both OLED and FED, permeabilities of  $\leq$  0.001 cc/m<sup>2</sup>\*day for oxygen, and  $\leq$  0.001 g/m<sup>2</sup>\*day for moisture (water vapor) are required.

15 20 25 A polymer OLED and small molecule OLED describes the layer that emits light in the OLED. For polymer OLED's, the light emitting material that is made by flow coating, spin coating, gravure coating, meniscus coating, curtain coating or any common liquid coating techniques, but the active layer of the display can also be processed with atmospheric coating if OLED is a polymer. ITO has been deposited by non vacuum processes such as by screen printing. Consequently, the process of the present invention can be entirely non vacuum, or alternatively a vacuum and non vacuum process. Preferably, the process is done in a vacuum because contamination by particulates is avoided. Superior barrier films and other films are provided by the cleaner vacuum process. Small molecule OLED are also typically vacuum deposited.

30 As shown in FIGS. 10 and 11 for the LCD, as long as the sheet resistance is below about 250 ohms/square, and as long as the ITO film thickness is between about 75 and 225 nm, the water permeability requirements for the LCD are met. As shown in FIG. 12, the oxygen permeability requirements for the LCD are met as long as the ITO film thickness is above about 85 nm and as long as the sheet resistance is below about 150 ohm/square. Because of the lower permeabilities required for the emissive displays (OLED and FED), multilayer dielectric or TCO barriers in combination with PML processed polymer coatings (i.e. composite barrier layers of PML deposited organic polymer layers, dielectric layers and/or TCO layers) are required.

5 Appendix D illustrates water vapor and oxygen permeability versus ITO thickness. The differences between semi-reactively and reactively sputtered ITO, as well as the differences between a single ITO layer and two ITO layers (with a polymer layer in between) are illustrated. 'Semi-reactively' sputtered refers to DC magnetron sputtered from a ceramic target, see Appendix C.

10 The preferred thickness for ITO is different for conductivity and barrier properties. The film thickness must be greater to have conductive properties. Also, if the layer is too thin it will not have barrier properties. The critical thickness for these layers varies with the material and to how the layer is deposited. For ITO, the critical minimal thickness is about 10 nanometers (or 100 angstroms). The lower limits for some of the metal oxides are about 10 to 30 nanometer range in packaging. Generally, 5-10 nanometers is the minimum thickness required for adequate barrier properties, however, 15 the film needs to be thicker for conductivity properties (20 nanometers to 300 nanometers). If thicker than that range, then the film starts cracking, and hence, loses conductivity. For maximizing optical transmission, it is well known that optical thicknesses of thin films can be selected. The typical physical thickness is 20-300 nanometers for ITO on a flexible substrate.

20 FIGs. 14 and 15 show that the PET substrates have lower sheet resistance and resistivity for the same oxygen flow rates than a glass substrate. FIG. 14 discloses a chart showing sheet resistance of various substrates versus oxygen flow rate through the respective substrate. Substrates of polyethylene terephthalate (PET), hardcoated PET (a PET coated with a base coat that is liquid smoothed/atmospheric coated for 25 surface abrasion resistance), and glass were compared. Glass has the highest sheet resistance, especially at oxygen flow rates over 3 sccm (standard cubic centimeters per minute). The chart shows that the glass sheet resistance reached approximately 500 ohms/square at an oxygen flow rate of 5 sccm. At the same oxygen flow rate, PET and hardcoated PET have approximately the same sheet resistance. The least sheet 30 resistance (35 ohms/square) for the PET substrates is at an oxygen flow rate of 2 sccm, while the highest sheet resistance (170 ohms/square) is at an oxygen flow rate of 5 sccm. FIG. 15 shows similar results for resistivity.

35 FIGs. 16 and 17 disclose charts showing sheet resistance and resistivity of various substrates versus oxygen flow rate through the respective substrate, where 7.5% of the plasma used in the sputtering process is hydrogen gas, respectively.

Substrates of polyethylene terephthalate (PET), hardcoated PET, and glass were compared. Again, glass has higher sheet resistance and resistivity, especially at oxygen flow rates over 3 sccm. The chart shows that at an oxygen flow rate of 5 sccm, the glass sheet resistance reached approximately 350 ohms/square and a resistivity of approximately  $27 \text{ ohms} \cdot \text{cm} \times 10^4$ . PET and hardcoated PET have approximately the same sheet resistance and resistivity for the same oxygen flow rate. The least sheet resistance (40 ohms/square) for these PET substrates is at an oxygen flow rate of approximately 2.3 sccm, while the highest sheet resistance (150 ohms/square) is at an oxygen flow rate of 5 sccm.

FIGs. 18 and 19 disclose charts showing sheet resistance and resistivity of various substrates versus oxygen flow rate through the respective substrate, where 20% of the plasma used in the sputtering process is hydrogen gas, respectively. Substrates of hardcoated PET, and glass were compared. Again, glass has higher sheet resistance and resistivity, especially at oxygen flow rates over below 2 sccm and 5 sccm. The oxygen flow rate for the hardcoated PET substrate did not exceed 6 sccm. Generally, the sheet resistance and resistivity are significantly lower for the increased percentage of hydrogen in the plasma, for oxygen flow rates above 3 sccm.

As can be seen for FIGS. 21-24, generally, regardless of the sheet resistance, the percentage of spectral transmittance and reflectance remains relatively constant. For example, at about a plasma wavelength of 500 nm, the transmittance percentage is about 80% for resistance ranging from 29 ohms/square to 347 ohms/square. DC sputter deposited ITO on a handcoated PET substrate exhibited a resistivity of 46.9 Ohms/square, which is approximately  $5 \times 10^4 \text{ ohm} \cdot \text{cm}$ , and a visible transmittance of 84.7%. Generally, the transmittance increases (and the reflectance decreases) as the plasma wavelength increases. A compromise between high optical transmittance and high conductivity is always required. For more on plasma wavelength, see Appendix C. In contrast, for FIG. 20 (a more preferred embodiment of the present invention), at the higher wavelengths, the transmittance decreases (and the reflectance increases).

Appendix E illustrates the Transmittance and Reflectance of semi-reactively sputtered ITO on a PET substrate for various thicknesses versus plasma wavelength. The transmittance and reflectance of a substrate coated with a polymer layer and an ITO layer, a substrate with an ITO layer, and a substrate with two ITO layers (with a

polymer layer in between the two ITO layers) are illustrated. Generally, transmittance and conductivity are inversely related.

5 For a transparent electrode, the conductivity requirements vary with display technology and addressing method. The visible transmittance for LCD's is about 90%, and for OLED's is about 80-85%. The surface resistivity for LCD's is about 50-300 ohm/square, and for OLED's is about 10-100 ohm/square. The thickness of the conductor layer is compatible with the web processing for the flexible plastic substrate.

10 Table 1 shows the test results for oxygen and water vapor transmission rates of various samples of a substrate coated with a single ITO layer with different ohm/square coatings and a substrate coated with an ITO layer, a metal layer, and another ITO layer.

15 The test conditions were as follows: the temperature was at 23°C/73.4°F. On each side of the barrier for the oxygen transmission rate tests, the relative humidity was 0%. On one side of the barrier for the water vapor transmission rate tests, the relative humidity was 100%, but the other side of the barrier had a relative humidity of 0%.

20 The first eight samples are a single layer ITO coated onto a plastic substrate with different resistances. For example, the '25-1' is the first sample of the resistance of 25 ohm/square; whereas '25-2' is the second sample from the same lot. The last two samples are of a substrate coated with an ITO layer, a metal coating, and another ITO layer, with a resistance of 10 ohm/square. This 3 layer configuration is called "optically enhanced metal," and has similar characteristics as a single TCO layer. With the optically enhanced metal good conductivity, transmission and barrier properties are achieved. Preferably the ITO layer has a thickness of about 50-60 nanometers. In 25 several instances, the samples were tested two times. The second column for the 25 and 60 ohm/square reflects the results of the second test.

Table 1

Sample	Water Vapor Transmission Rate (g/m <sup>2</sup> *day)		Oxygen Transmission Rate (cc/m <sup>2</sup> *day)	
25-1	0.026	<0.005 <sup>1</sup>	0.017	0.087
25-2	0.097	<0.005 <sup>1</sup>	0.584	0.257
60-1	0.042		0.059	0.071
60-2	0.050		0.204	0.090
60-3	0.007		<0.005 <sup>2</sup>	
60-4	<0.005 <sup>1</sup>		0.014	
300-1	0.243		0.861	
300-2	0.232		0.864	
M-10-1	0.076		0.035	
M-10-2	0.041		0.024	

1 The actual water vapor transmission rate was at least as low as the lower limit of the instrument, Permatran-W 3/31, 0.005 g/m<sup>2</sup>\*day .

2 The actual oxygen transmission rate was at least as low as the lower limit of the instrument, Ox-Tran 2/20, 0.005 cc/m<sup>2</sup>\*day.

5 Table 2 compares permeation rates for different coatings, including multiple dyad (an acrylate/oxide pair) layers, on polyethylene terephthalate (PET) and oriented polypropylene (OPP) substrates. As can be seen, a single dyad on a substrate has high permeation resistance for oxygen and moisture. In some instances, two oxygen transmission rate tests were conducted, and the results were shown in a second column. <sup>1</sup> denotes the typical permeation rate for the PET substrate.

Table 2

Sample	Water Vapor Transmission Rate (g/m <sup>2</sup> *day)	Oxygen Transmission Rate (cc/m <sup>2</sup> *day)	
2 mil PET	30.5, 272 <sup>1</sup> per micron film thickness	5.3, 1550 <sup>1</sup> per micron film thickness	
Food packaging - target values (PET/oxide)	1.55	1.5	
2 mil PET/single dyad (23°C)	<0.0078	0.03	
2 mil PET/ seven dyads (23°C)	<0.0078	<0.016	
7 mil PET/ hardcoat (23°C)	7.6	-	
7 mil PET/ hardcoat/ single dyad (38°C)	<0.0078, 90% Relative Humidity (RH), 100% O <sub>2</sub>	0.2682, 100% RH	0.6061, 100% RH
7 mil PET/ hardcoat/ single dyad/ ITO (38°C)	<0.0078, 90% RH, 100% O <sub>2</sub>	0.0098, 100% RH	0.0128, 100% RH
PET/oxide	0.7-1.5	0.15-0.9	
PET/AI	0.6	0.17	
OPP, copolymer, 1 mil	1800	1.3	
OPP/ oxide	17-546	0.08-0.4	
OPP/AI	20	0.11	

Table 3

Sample	Water Vapor Transmission Rate (g/100in <sup>2</sup> *24 hours)	Oxygen Transmission Rate (cc/100in <sup>2</sup> *24 hours)
A	<0.001	<0.001
B	<0.001	<0.001
C	<0.001	<0.001
D	<0.001	<0.001
E	0.369	1.971
F	0.370	1.934
G	0.340	1.834
H	0.377	1.888

5 Samples A through D are layers of polymer (PML)/oxide/polymer (PML) on 2 mil PET. Samples E through H are 2 mil PET only.

10 Although the present invention has been described and is illustrated with respect to various embodiments thereof, it is to be understood that it is not to be so limited, because changes and modifications may be made therein which are within the full intended scope of this invention as hereinafter claimed. In particular, the structure disclosed for flat panel displays can also be used with other display technologies, such as polymer light emitting diode (PLED) and light emitting diode (LED) displays.